Multicomponent Percolation Criterion and its Application to Hopping in Disordered Conductors

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An approximate percolation criterion for the multicomponent problem (when a condition of connectedness depends on the "colors" of sites) is proposed and its relation to mean-field theory is established. Its accuracy is discussed for several colored random-site- and lattice-percolation models. An application to hopping allows for an approximate solution of various problems: e.g., the hopping conductivity in the range intermediate between the nearest-neighbor hopping and the variable-range hopping regimes can be found for arbitrary shape of the density of states.

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The percolation problem [1] is usually formulated on a lattice, where a fraction of randomly chosen bonds (bond problem), or sites (site problem) are destroyed (see reviews [2]). Some generalizations of lattice percolation for "polychromatic" models (with several sorts of sites or bonds) were proposed, but their properties have been described only in the few simplest cases [3,4]. There are special percolation problems formulated on a set of sites randomly distributed in space. One application of random-site percolation is hopping—an incoherent transport of electrons via randomly distributed impurities [5]. Here multicomponent generalizations occur very naturally (e.g., variable-range hopping [5,6]). An approximate percolation criterion for one special multicomponent random-site model was proposed in [7]. Nevertheless, as in the case of lattice percolation, no general approach to "colored" random-site percolation exists. The aim of this Letter is to introduce such an (approximate) approach for both random-site and lattice problems.

Random-site percolation.—Consider randomly distributed sites of concentration N. The condition of connectedness of two sites i and j is $\xi(\mathbf{r}_i - \mathbf{r}_j) < \xi$, where $\xi(\mathbf{r})$ is a connectivity function. Let us vary the parameter ξ, keeping an eye on connected sites. At low ξ there are only rare small clusters, while at large ξ almost all sites are connected in one infinite cluster. Hence at some critical $\xi = \xi_{\text{crit}}$, an infinite cluster must appear for the first time, and a fraction of sites involved in it vanishes at $\xi = \xi_{\text{crit}}$.

An average number of bonds for any given site is $B(\xi) = NV(\xi)$, where $V(\xi) = \int_{\xi(\mathbf{r})<\xi} d\mathbf{r}$ is a volume of D-dimensional figure $\Xi(\xi)$ restricted by the condition of connectedness. The percolation is established when B reaches some critical value:

$$B(\xi_{\text{crit}}) \equiv NV(\xi_{\text{crit}}) = B_{\text{crit}}\,. \tag{1}$$

For the isotropic case [spherical $\Xi(\xi)$], numerical calculations [8,5] have given $B_{\text{crit}}^{(D=3)} \approx 2.7$ and $B_{\text{crit}}^{(D=2)} = 4.5$. In the anisotropic case, B_{crit} may, in principle, depend on the shape of $\Xi(\xi)$. Numerical studies [8,9] have, however, revealed a remarkable shape invariance of B_{crit}, which gave birth to an approximate "invariant method" [5,8,9].

Suppose now that we have several classes of sites (labeled by a color index c), randomly distributed with partial concentrations N_c (the total concentration $N = \sum_c N_c$). The connectedness condition for sites i and j depends now on their colors: $\xi_{c_i c_j}(\mathbf{r}_i - \mathbf{r}_j) < \xi$. Strictly speaking, there is no general approach to this class of problems, since the properties of the infinite cluster may depend on the structure of the connectivity matrix $\xi_{cc'}(\mathbf{r})$. In what follows, we propose, however, such a general (though approximate) approach that takes care of only one rough property of the infinite cluster—its color composition $\tilde{N}_c$.

Let us define *active* bonds of any given site as all links that connect this site with those other sites (irrespective of their color) that *belong to the infinite cluster.* Then an average number of active bonds for a site of color c is $\tilde{B}_c = \sum_{c'} \tilde{N}_{c'} \int_{\xi_{cc'}(\mathbf{r})<\xi} d\mathbf{r}$. Our basic assumption is that the probability $P_c \equiv \tilde{N}_c/N_c$ for a site (of color c) to belong to the infinite cluster depends *only* on such a rough characteristic as $\tilde{B}_c$. Then the color composition of the infinite cluster $\tilde{N}_c$ is governed by a system of equations, $\tilde{N}_c = N_c F(\tilde{B}_c)$. Close to the percolation threshold the universal function $F(\tilde{B})$ may be expanded: $F(\tilde{B}) \approx a\tilde{B} - b\tilde{B}^2$, and we arrive at the system of quadratic equations

$$\tilde{N}_c = c\tilde{B}_c - b\tilde{B}_c^2\,. \tag{2}$$

If $a, b > 0$, then for $\xi < \xi_{\text{crit}}$, there is only the trivial nonnegative solution $\tilde{N}_c \equiv 0$, while at $\xi = \xi_{\text{crit}}$ a nontrivial solution appears:

$$\tilde{N}_c(\xi) \propto (\xi - \xi_{\text{crit}})\tilde{N}_c^{(\text{crit})}. \tag{3}$$

The threshold ξ_{crit} is determined by a condition $NV_{\text{eff}}(\xi_{\text{crit}}) = 1/a$, where $V_{\text{eff}}(\xi)$ is the maximal eigenvalue of the matrix

$$A_{cc'}(\xi) = n_c \int_{\xi_{cc'}(\mathbf{r})<\xi} d\mathbf{r}, \quad n_c = N_c/N\,, \tag{4}$$

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and the vector $\tilde{N}_c^{(\mathrm{crit})}$ in Eq. (3) is the corresponding eigenvector. Comparing our condition with (1) in the colorless case, we find $a = 1/B_{\mathrm{crit}}$, and finally our approximate percolation criterion reads

$$NV_{\mathrm{eff}}(\xi_{\mathrm{crit}}) = B_{\mathrm{crit}}\,. \tag{5}$$

The crucial point of the above arguments is that only the *active* bonds should be counted. Different bonds contribute to the average connectedness criterion with a weight $\tilde{N}_c$, which has yet to be determined self-consistently and, in general, does not have to coincide with the trivial one N_c. The "naive criterion," counting *all* bonds, would lead to manifestly incorrect results for cases with a strong color dependence. Generally, the criterion (5) always somewhat underestimates the percolation threshold, while the naive one overestimates it. For example, in the variable circles model (see [8]) our criterion gives the critical concentration of circles 7.4% less than the simulations result, while the naive one overestimates it by 13.5%.

The form of the function $V_{\mathrm{eff}}(\xi)$ depends only on the structure of $\xi_{cc'}(\mathbf{r})$ and on the partial concentrations n_c. All the necessary information about the structure of the percolation cluster is accumulated in the constant B_{crit}, which is postulated to be the same as in the *colorless* case. Thus our procedure is an approximate mapping of the colored percolation cluster onto an effective colorless one. It is a generalization of the invariant method, also implying the mapping of an *anisotropic* percolation cluster onto an effective *isotropic* one.

There is a simple connection between our approach and the mean-field theory (see [2,5]). Indeed, introducing a multicomponent order parameter $\tilde{N}_c$ and writing an effective free energy $\mathcal{F}$ near the percolation threshold as

$$\mathcal{F} = \sum_{cc'} \alpha_{cc'}(\xi)\tilde{N}_c\tilde{N}_{c'} + \sum_{cc'c''} \beta_{cc'c''}(\xi)\tilde{N}_c\tilde{N}_{c'}\tilde{N}_{c''} + \cdots,$$

we find ξ_{crit} as the point where a minimal eigenvalue of the matrix $\alpha_{cc'}(\xi)$ vanishes. The equations for $\tilde{N}_c$, providing a minimum to the free energy, may be identified with Eq. (2), if $\alpha_{cc'}(\xi) \to [B_{\mathrm{crit}}\delta_{cc'}/N_c - V_{cc'}(\xi)]$. The solution (3) is also of a mean-field type, and the index $\beta = 1$ [$N_c \propto (\xi - \xi_{\mathrm{crit}})^{\beta}$] is exactly the mean-field one. The phenonenological Landau theory itself is unable to specify the structure of $\alpha_{cc'}(\xi)$, while the present approach gives an *explicit form* of the matrix $\alpha_{cc'}(\xi)$, which allows one to find the critical point ξ_{crit} and to single out the critical mode $\tilde{N}_c^{(\mathrm{crit})}$.

Lattice percolation.—Consider a colored lattice, where each site has a color c, with probability n_c ($\sum_c n_c = 1$), and the probability $p_{c_ic_j}$ of the bond occurrence within a pair $\langle ij\rangle$ of the neighboring sites depends on their colors. Introducing $\tilde{N}_c$ and $\tilde{B}_c$ by the analogy with the random-site case, and repeating our arguments, we arrive at Eq. (2) with $\tilde{B}_c = z\sum_{c'} p_{cc'}\tilde{N}_{c'}$ (z being the lattice coordination number), and find the percolation criterion

$$x_{\mathrm{eff}}(\{n\}, \hat{p}) = x_{\mathrm{crit}}\,, \tag{6}$$

where x_{eff} is the maximal eigenvalue of the matrix $A_{cc'} = n_c p_{cc'}$. The value $x_{\mathrm{crit}} = 1/za$ may be chosen to give the correct result for the standard site problem, which is a bicolored version of the present extended model with $p_{12} = p_{21} = p_{22} = 0$, $p_{11} = 1$. For this model one finds $x_{\mathrm{eff}} = n_1 = x^{(\mathrm{site})}$, so x_{crit} may be identified with the critical concentration $x_{\mathrm{crit}}^{(\mathrm{site})}$ of the site problem. Then the criterion (6) gives the correct result also for Zallen's model of polychromatic percolation [3], for which $p_{cc'} = \delta_{cc'}$. Its exactness in this case is natural, because here the infinite cluster consists always of sites of the same color.

The standard *bond* problem is a colorless version of the extended model. Here $x_{\mathrm{eff}} = p_{11} = x^{(\mathrm{bond})}$; thus our criterion predicts the coincidence of the critical concentrations for both standard versions of the percolation problem on any given lattice: $x_{\mathrm{crit}}^{(\mathrm{bond})} = x_{\mathrm{crit}}^{(\mathrm{site})}$. The accuracy of this relation is good for low-z lattices: 7% for the honeycomb lattice ($z = 3$), 9% for the diamond lattice ($z = 4$). It becomes poorer, when z increases: 25% for the sc lattice ($z = 6$), 60% for the fcc lattice ($z = 12$). The discrepancy indicates a difference in the geometry of percolation clusters for both problems due to bond correlations, present in the site problem.

In the AB percolation model (see [4]) the sites of *opposite* colors are linked in the bicolored lattice ($p_{AA} = p_{BB} = 0$, $p_{AB} = p_{BA} = 1$). The criterion (6) gives $x_{\mathrm{crit}}^{(\mathrm{site})} = \sqrt{n_{\mathrm{crit}}(1 - n_{\mathrm{crit}})}$, where n_{crit} is the value of n_A at which AB percolation occurs. From this relation it follows, in particular, that AB percolation is impossible in lattices with $x_{\mathrm{crit}}^{(\mathrm{site})} > 1/2$. Note that for bipartite lattices this statement is rigorous [4]. Numerical simulations of AB percolation in the sc lattice give $n_{\mathrm{crit}} \approx 0.143$ [4], while our criterion gives $n_{\mathrm{crit}} \approx 0.109$, which is 24% less.

Applications to hopping.—The standard problem of hopping can be reduced to the colored random-site percolation, where the color c_i is identified with an electronic level ε_i of impurity i, and the connectivity matrix has the form [5]

$$\xi_{\varepsilon\varepsilon'}(\mathbf{r}) = \frac{2r}{a_B} + \frac{E(\varepsilon,\varepsilon')}{T}\,,$$

$$E(\varepsilon,\varepsilon') = \frac{|\varepsilon| + |\varepsilon| + |\varepsilon - \varepsilon'|}{2}\,,$$

T being the temperature, and a_B being the Bohr radius of an impurity state. According to Eq. (4), we arrive at a linear integral operator with a kernel

$$A(\varepsilon,\varepsilon') = n(\varepsilon)v(\xi - E(\varepsilon,\varepsilon')/T)\,,$$

where $n(\varepsilon) = N(\varepsilon)/N$ is the normalized density of states, and $v(x) = (\pi/2D)(ax)^D\theta(x)$. The average resistivity $\rho \propto \exp(\xi_{\mathrm{crit}})$, so calculating the maximal eigenvalue of $A(\varepsilon,\varepsilon')$ and then applying the criterion (5) one can, in principle, find ρ for arbitrary T and $N(\varepsilon)$.

In the high-T_c nearest neighbor-hopping limit, when $E(\varepsilon,\varepsilon')/T\xi^{(0)} \ll 1$ and $\xi^{(0)} = (1/a_B)(2DB_{\mathrm{crit}}/\pi N)^{1/D}$,

the perturbative approach ($\xi_{\rm crit} = \xi^{(0)} + \xi^{(1)} + \xi^{(2)} + \cdots$) can be used. In the first order it gives $\xi^{(1)} = \varepsilon_3/T$, with an activation energy of the nearest-neighbor hopping $\varepsilon_3 = \langle\langle E(\varepsilon,\varepsilon')\rangle\rangle_{\varepsilon\varepsilon'} \equiv \int d\varepsilon\, d\varepsilon'\, n(\varepsilon)n(\varepsilon')E(\varepsilon,\varepsilon')$, coinciding with the result of [10]. The second-order correction

$$\xi^{(2)}_{\rm crit} = -\frac{D-1}{2}\frac{\langle\langle\tilde{E}(\varepsilon\varepsilon')^2\rangle\rangle_{\varepsilon\varepsilon'}}{\xi^{(0)}T^2} - D\frac{\langle\langle\langle\tilde{E}(\varepsilon\varepsilon')\tilde{E}(\varepsilon'\varepsilon'')\rangle\rangle\rangle_{\varepsilon\varepsilon'\varepsilon''}}{\xi^{(0)}T^2}$$

(where $\tilde{E} = E - \varepsilon_3$) consists of two parts. The first term is the result of first-order perturbation theory, applied to the second correction to $\hat{A}$; it does not involve any corrections to the composition $\tilde{N}_c$ and coincides with the result of the naive approach [5,11]. The second term is the result of second-order perturbation theory, applied to the first correction to $\hat{A}$. It is due to corrections to the composition, $\tilde{N}(\varepsilon) \propto n(\varepsilon)\{1 - D\frac{\langle\tilde{E}(\varepsilon,\varepsilon')\rangle_{\varepsilon'}}{\xi_0 T} + \cdots\}$, and is lacking in the naive approach. This term reflects a tendency to adapt a composition of the infinite cluster: Impurities with high energies $|\varepsilon|$ may be forced out of the infinite cluster due to their poor connectivity (positive $\tilde{E}$), while impurities with low $|\varepsilon|$ (negative $\tilde{E}$) may increase their representation. Therefore the true value of $\xi_{\rm crit}$ must be lower than in the naive approach. In agreement with the conjecture [5,10], $\xi_{\rm crit}$ may be expanded in momenta and correlators of $E(\varepsilon,\varepsilon')$. While the first correction $\xi^{(1)}$ is exact, the numerical coefficients in both second-order terms are not approximation-free; they depend on the form of the approximate criterion (5).

At low temperatures the variable-range-hopping regime [6,5] is developed, in which only levels within a narrow energy strip, $|\varepsilon| < \Delta_{\rm Mott}(T) = T\xi_{\rm crit}$, contribute to the infinite cluster. A rigorous approach [5,12] to this case leads to a special percolation problem in $D+1$ dimensions and

$$\xi_{\rm crit} = (T_0/T)^{1/(D+1)}, \quad T_0 = \beta/N(0)a_B^D. \tag{7}$$

Numerical simulations [5,13] have given the constants $\beta_{D=3} \approx 21.2$ and $\beta_{D=2} \approx 13.8$. Let us demonstrate that the criterion [Eq. (5)] reproduces the form of Eq. (7) and gives a good approximation for the constant β. Introducing dimensionless variables $x \equiv \varepsilon/T\xi$, we find

$$V_{\rm eff}(\xi) = \frac{\pi}{2D}\frac{N(0)}{N}Ta_B^D\xi^{D+1}\Lambda_D \tag{8}$$

where $\Lambda_{D=3} \approx 0.315$, $\Lambda_{D=2} \approx 0.430$ are maximal eigenvalues, found numerically, of linear operators with kernels $h_D(x,x') = [1 - E(x,x')]^D\theta(1 - E(x,x'))$ (the corresponding eigenfunctions are shown in Fig. 1). Substituting Eq. (8) into the criterion (5), we arrive at the expression (7) with $\beta = 2DB_{\rm crit}/\pi\Lambda$, which gives $\beta_{D=3} \approx 16.4$ (23% less than the simulation result), and $\beta_{D=2} \approx 13.3$ (4% less than the simulation result). In fact, the accuracy of simulations in two dimensions (2D) is higher than in 3D, and therefore we expect the actual accuracy of our approximation to be closer to 4% rather than to 20%. Note that the naive criterion, implying that all the energies within the Mott strip contribute to the infinite cluster with the same weight, would give values of β 65% higher than the numerical ones for both $D = 3$ and $D = 2$. The reason for such an overestimation is clear: The actual energy distribution $\tilde{N}(\varepsilon)$ is much narrower than the naive one (see Fig. 1). So our method, being an exact one in the nearest-neighbor-hopping regime, shows good accuracy also in the opposite—variable-range-hopping—limit. Therefore we expect it to work well also in the intermediate-T range.

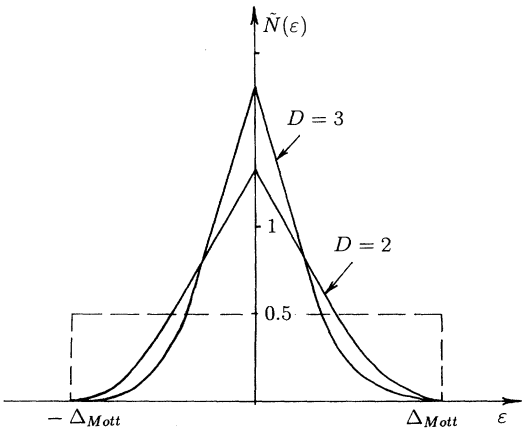

FIG. 1. Normalized energy distribution $\tilde{N}(\varepsilon)$ for sites belonging to the infinite percolation cluster in the variable-range-hopping problem: $\Delta_{\rm Mott}$, the width of the Mott's strip. Broken line, the naive approach; full lines, the present approach (for spatial dimensions $D = 2$ and $D = 3$).

Shklovskii and Efros (see [5], p. 343) have introduced a different percolation criterion, also giving the constant $\beta^{(D=3)}$ with high accuracy: They have postulated the average volume fraction, $\Theta = \langle\pi r_{ij}^3/6\rangle_{\rm bonds}$, to be invariant instead of the average number of bonds $B = \langle 1\rangle_{\rm bonds}$, and applied the naive approach to this invariant Θ. In principle, their criterion may be improved by taking into account only the *active* bonds: $\Theta \to \tilde{\Theta} = \langle\pi r_{ij}^3/6\rangle_{\rm active\ bonds}$, and by repeating our arguments, applied to $\tilde{\Theta}$ instead of $\tilde{B}$. This would make the criterion more reliable than it is in its naive form. On the other hand, it would also lower the predicted value of β, destroying the agreement with numerical data. This fact makes us think that it is B invariant, rather than Θ invariant, that can serve as the starting point for the approximate percolation criterion.

The same arguments may be addressed to the criterion of Butcher and Hayden [14]. They have applied the naive approach to the invariant B, but the "constant" $B_{\rm crit}$ they have regarded as a function of T, interpolating between $B_{\rm crit}^{(D)}$ at high T and $B_{\rm crit}^{(D+1)}$ at low T (since the energy ε constitutes an additional dimension). The improved criterion (5) demonstrates, however, a much

better accuracy for $B_{\rm crit} = B_{\rm crit}^{(D)}$ than for $B_{\rm crit} = B_{\rm crit}^{(D+1)}$, even for low T, indicating that the variable-range-hopping percolation is rather effectively D dimensional.

For hopping with different sorts of impurities additional colors of sites arise. In the model studied in [7], the spin of electrons at each impurity was rigidly oriented. The impurities belonged (with the same probability) to two sublattices with opposite spin orientations, so that intersublattice hops (involving spin-flip processes) were relatively suppressed, and one had the connectedness criterion $\xi_{\varepsilon c \varepsilon' c'}(\mathbf{r}) = \xi_{\varepsilon\varepsilon'}(r) + \Delta_{cc'}$, with additional color $c = 1, 2$, and with $\Delta_{11} = \Delta_{22} = 0$, $\Delta_{12} = \Delta_{21} = \Delta$. The present method enables one to consider arbitrary concentrations N_1, N_2 of impurities in sublattices. It leads to a system of two linear integral equations with the kernel

$$A_{cc'}(\varepsilon, \varepsilon') = n_c(\varepsilon) v(\xi - \Delta_{cc'} - E(\varepsilon, \varepsilon')/T).$$

There is a surface (determined by the condition $\xi_{\rm crit} = \Delta$) in the (T, N_1, N_2) space, separating the domains of the bicolored regime (high resistance, low N, T) and the single-colored one (low resistance). At very low concentrations (deep in the bicolored regime) the impurities of both sublattices participate in the infinite cluster with their "natural" weight N_c. Upon increasing N, the discrimination of the sublattices occurs, and, finally, at $N > N_{\rm crit}$, the intersublattice hops are totally suppressed, the percolation cluster consists of one dominant color only, and $\xi_{\rm crit} = \xi_{\rm crit}(\max(N_1, N_2))$.

Recently the problem of hopping with an additional color arose in connection with a system where a double occupancy of impurities is allowed [15]. Our criterion, being applied to this problem, would also lead to a system of two coupled linear integral equations.

In conclusion, we consider the high accuracy of our method in the applications discussed as an indication that the percolation clusters in these cases do not differ much from the colorless one. Counterexamples, of course, also exist, but even there our theory gives qualitatively correct results. The quantitative accuracy of our criterion may be *ad hoc* improved by the proper choice of a reference model: One should choose an appropriate simple percolation model, whose solution is known, and map a more complex problem onto it. For example, we could have normalized the lattice version of our criterion by the bond problem rather than by the site problem.

The field of possible applications of the present method is vast. We mention here only the properties of island films and polydisperse composites, polycrystalline growth, and dynamics of random populations.

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